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MASS SPECTROMETRY MEASUREMENTS OF THE COMPOSITION OF THE LOWER
ATMOSPHERE OF VENUS

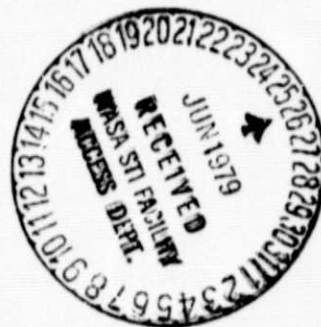
By

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Moscow, Report, 1978, 15 pages



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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MASS SPECTROMETRY MEASUREMENTS OF THE COMPOSITION OF THE LOWER ATMOSPHERE OF VENUS

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Mass spectrometers were part of the scientific equipment installed on the descent vehicles of the Venera-11 and Venera-12 spacecraft. The task of the mass spectrometer measurements was precision in data on the chemical composition of the lower atmosphere of Venus in particular of the basic components, measurement of the content of small admixtures of the atmosphere (particularly the content of rare gases) and, finally, determination of the isotope state of the basic components (carbon, oxygen, nitrogen) and the inert gases. /1*

The first report on the results of the mass spectrometer experiment in the dense atmosphere of Venus has already been published (Istomin *et al.*, 1970). This report contained data on approximate analysis of only part of the mass spectrometer information obtained, processed using calibrations made ahead of time. In this report, there are results on a more complete analysis of the material obtained which is based, again only on the data of preflight calibrations of the equipment. A more complete survey of the material supports the data of preliminary analysis and leaves **the figures given for concentrations** of all recorded components practically unchanged. This applies also to the data on **the isotope state, primarily,** data on the isotopes of argon. One should add that at the moment this report is being prepared we have just begun to know the first results of the experiments made on the Pioneer-Venus mission so that a certain amount of attention will be given here separately to considering **the results** and their compilation.

*Numbers in the margin indicate pagination in the foreign text.

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A mass spectrometer used on the Venera-11 and Venera-12 spacecraft was created as a result of further development of work done in this direction in the Soviet Union (Istomin et al., 1975). The method and equipment of the experiment will be described in detail in subsequent publications.

The method of the experiment included using a mass analyzer of a radio-frequency type which has average resolution by mass in combination with a pulse system of input of gas samples into the mass-spectrometer. A block diagram of the mass-spectrometer experiment is given in Figure 1. The atmospheric components, under the effect of pressure differences, occurring due to the high speed pressure with descent of the craft, freely passed through the cavity of the input valve which was connected to the atmosphere by two open turboconductors. During the time between sequential sampling of the gas, the cavity of the input valve was washed several times by the atmospheric components. Gas sampling from the cavity was accomplished by brief opening of the valve of the input. A carefully measured microportion of gas admitted into the mass-spectrometer was evacuated from the mass-analyzer using an ion-getter of the magnetic discharge high vacuum pump.

During the experiment, the mass-spectrometer was adjusted ahead of time automatically for input of the required portion of gas, sequentially increasing the controlling effect on the input valve. During the entire time of the scan, transmission of the mass-spectra was carried out in the same range of mass and the scan time of the spectrum was decreased to 1 second. Upon reaching the required input, the instrument was switched to the analysis regime during which, for each portion of gas, eight mass-spectra were transmitted after which the cycle was repeated. The instrument periodically could analyze inert gases with increased sensitivity. The sensitivity for the inert gas was increased by changing the operating procedure

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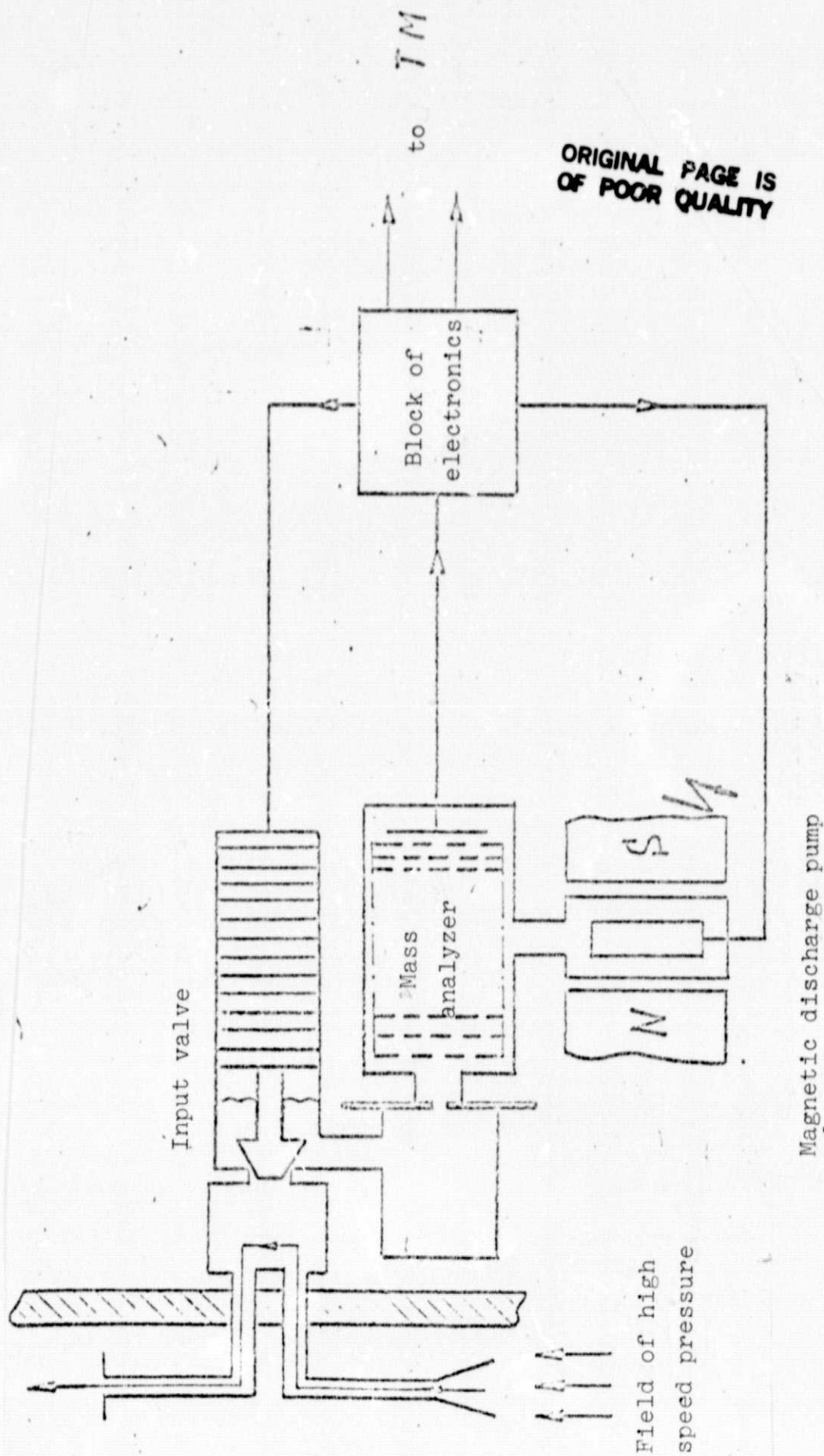


Figure 1. Block diagram of the mass-spectrometer experiment on the Venera-11 and Venera-12 descent vehicles.

of the magnetic discharge pump; here the rate of evacuation /3
of rare gases was decreased to zero while productivity of the
pump on chemically active gas (CO₂, nitrogen) remained practically
unchanged. The gain in sensitivity for rare gases due to
transferring the instrument to a "static" regime was about
20 times. All of the even cycles of operation of the mass-
spectrometers carried out the analysis regime for inert gases
with increased sensitivity.

The basic characteristics of the mass-spectrometer are
the following:

Range of mass numbers	11-105 amu
Resolution at the level of 0.1 amplitude of a mass- peak	= M/M = 35 _± 5
Scan time for a range of mass in the scanning regime	1 s
Scan time of a range of mass in the analysis regime	7 s
Sampling time for the gas	less than 5·10 ⁻³ s
Emission current	0.4 amp
Ionizing potential	40 V
Sensitivity (for small ad- mixtures in CO ₂ , per single spectrum):	
Nitrogen	0.2%
Neon, methane	5 ppm
Argon krypton	1 ppm
Weight	9.5 kg
Consumption	17 v-a

The mass-spectrometers on both descent vehicles took /4
their first sampling at an altitude of about 23 km and operated
up until landing. The last samples of gas were taken by the

mass-spectrometer at an altitude from 3 to 1.5 km over the surface of the planet. The mass-spectrometers on the descent vehicles of the Venera-11 and Venera-12 took 11 gas samplings, transmitted 176 mass-spectra to Earth which characterized the chemical and isotope composition of the lower atmosphere of Venus. The mass-spectra were transmitted and recorded in the same way, the amplifier of the ion current of the mass-spectrometer had 4 scales of sensitivity with coefficients of amplification 1, 10, 10^2 and 10^3 , a change in scale was made automatically at the mass-peak; due to this, the true telemetric recording of the spectrum has an "illegible" appearance. Examples of the mass spectra obtained are presented in drawings 2 and 3; these mass spectra will be commented on below.

Transmission of five control parameters of the mass-spectrometer preceded each mass-spectrum; these included emission current of the ion source and current of the magnetic discharge pump. These control parameters are visible on the spectra in Figure 2 in the form of characteristic "stages."

Both mass-spectrometers were identical inasmuch as this was possible and feasible both in their production process and in testing before installation on the vehicles and (in particular) according to electrical characteristics. In particular, a good deal of attention was devoted to the identical condition of the instruments in relation to the value of the emission currents and the ionizing potential and the "lag" potential. The magnitude of the latter determines resolution according to mass number of the analyzer of a radio-frequency type and as concerns the ionizing potential, this magnitude was selected so that in the mass-spectra there were no double peaks of ionized CO_2 (peak 22 amu) and argon (peak 20 amu).

The instruments which remained in the laboratory also

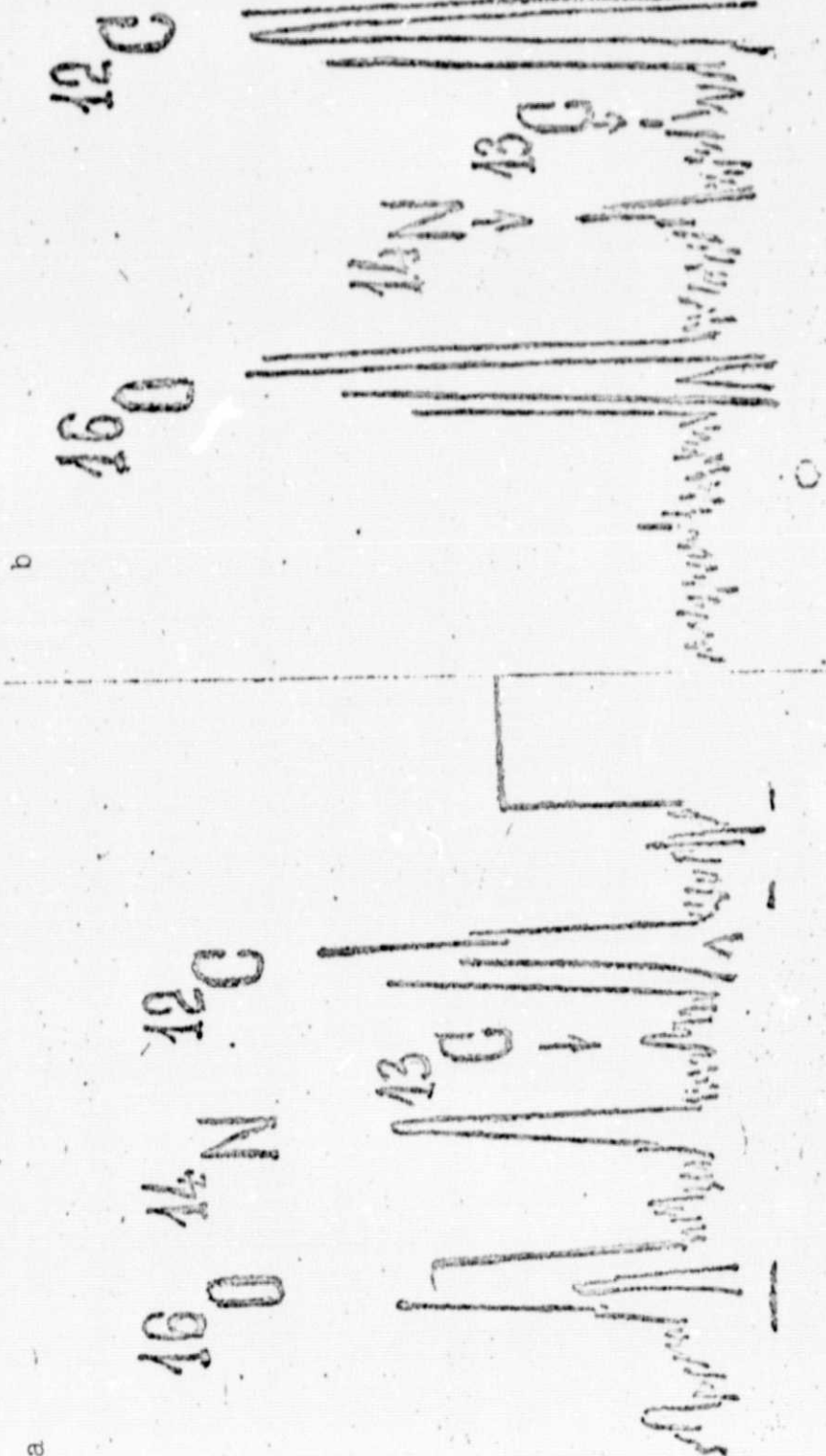


Figure 2. Fragments of the mass-spectra in the 12-16 amu field. On the left--a mass spectrum of the atmosphere of Venus (Venera-11), on the right--the mass-spectrum of the calibrated mixture containing 1.5% nitrogen. It is very clear that the peak with $M = 14$ (nitrogen) in the spectrum of the atmosphere of Venus has a much larger magnitude than in the spectrum of the calibrated mixture. (It is convenient to compare the peaks with $M = 14$ and $M = 13$ -- ^{13}C isotope).

were completely identical to those installed on the Venera-11 and Venera-12. A series of "preflight" calibrations was made on these instruments; the results were used for approximate analysis of flight data. The main volume of the calibrations was done using mixtures prepared on a CO₂ base with high degree of purity (about 99.998%); here the main admixture within this degree of purity was nitrogen. The content of inert gases in the initial CO₂, basically argon, did not exceed 0.2 ppm.

The basic model of the mixture was a mixture containing 1.5% nitrogen, 0.4% oxygen, 175 ppm argon and the remainder high purity CO₂. The mixture was prepared by thinning CO₂ in atmospheric air giving it a composition according to preparation. The second mixture used was a mixture with a content of nitrogen of about 4%. Calibration for neon and krypton were done according to atmospheric air.

As is described, the main source of system error of mass-spectrometer determination of the composition of the atmosphere of Venus, whose results are presented below, is error in knowledge of the composition of the model mixtures. It is submitted that an evaluation of +10-15% is optimistic so that the final results for the "basic" small components, nitrogen and argon, can be burdened with a systematic error of about 20%.

As to the components which were observed at maximum sensitivity (for a single spectrum)--as an example, neon and krypton, the error in determining them is roughly estimated to be on the order of $\begin{matrix} +100\% \\ -50\% \end{matrix}$.

The magnitudes of error indicated possibly will be decreased as a result of subsequent work in analyzing the data obtained.

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Results:

The basic admixture in the atmosphere of Venus, as the first mass spectra obtained showed is nitrogen. Its concentration amounts to approximately $4.5 \pm 0.5\%$. This figure was obtained by measuring the fragmentation peak with $M = 14$; it is confirmed by measurement on both vehicles and the spread of separate points in an overwhelming majority of cases is inside the error indicated. The results on nitrogen are illustrated by fragments of the mass-spectra in Figure 2, where spectra of the mass of the atmosphere of Venus and the model mixture with a content of nitrogen 1.5% are compared.

The figure presented, in general, is also confirmed by measurement of the peak with $M = 28$. The peak with $M = 28$ is the total of the mass-peaks of nitrogen and the fragmentation peak CO^+ which occurs as a result of dissociative ionization of the CO_2 electrons. In a case of measurement according to the peak with $M = 28$, the spread of separate experimental points, in a large number of cases, is outside the limits of the error indicated. The cause of this is being analyzed.

Concentrations of all the other admixtures in the atmosphere of Venus such as chemical-active and inert gases and vapors is below the level of a few hundredths of volumetric %.

Thus, mass-spectrometrically water vapor, chlorine and sulfur are detected almost at the limit of sensitivity of a single spectrum. Water vapor is in the "excess" peaks with $M = 18$ and $M = 17$, above the values caused by a "normal" isotope composition of the oxygen. Chlorine is detected on several mass-spectra as a weak peak with $M = 35$, and sulfur-- in the form of an "excess" of a mass-peak with $M = 32$, above the value caused by the input of O_2^+ ions in the ion source of the instrument, due to dissociation with ionization of CO_2 . In view of the fact that preliminary calibration of the

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mass-spectra for water, chlorine, sulfur and compounds of the two latter was not conducted, these data must be considered as especially preliminary. A quantitative evaluation of the content of small admixtures indicated cannot be made in this report.

However, one should make one more comment. In principle, the excess in the mass peak with M-32 can be recorded also in molecular oxygen in the atmosphere of Venus. The presence in the atmosphere of Venus of vapors of sulfur is much more probable than the presence of free oxygen. However, in light of the latest data of chromatographic measurement by Oyama (1979), according to which molecular oxygen was detected in the lower atmosphere of Venus in concentrations of about 60 ppm, the recorded excess in the mass-peak with $M = 32$ can, with a certain stretch, be explained also by free O_2 . In any case, whatever the possible identification is, it is still necessary that optical spectrophotometric measurements conducted simultaneously on the Venera-11 and Venera-12 craft (Moroz et al., 1979) establish an extremely low upper limit for gaseous sulfur in the lower atmosphere of Venus. However, these same optical measurements **cause doubt** about the interpretation of the "excess" of the mass-peak of $M = 18$ presented above.

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The mass-spectrometer recorded a series of inert gases in the atmosphere of Venus, namely, three isotopes of argon (36, 38 and 40 amu), neon (20 amu) and krypton (84 amu). The isotopes of argon are clearly visible on the fragment presented of the mass-spectrum in Figure 3. It is clear that the isotope composition of argon is sharply "abnormal," in comparison with the argon in Earth's atmosphere. The abundance of "secondary" (radiogenic isotope A40) in the atmosphere of Venus equals the total abundance of "primary" isotopes A36 and A38. As is known, in the atmosphere of Earth, the isotope A40 is 300 times more plentiful than the A36 isotope. The relative abundance

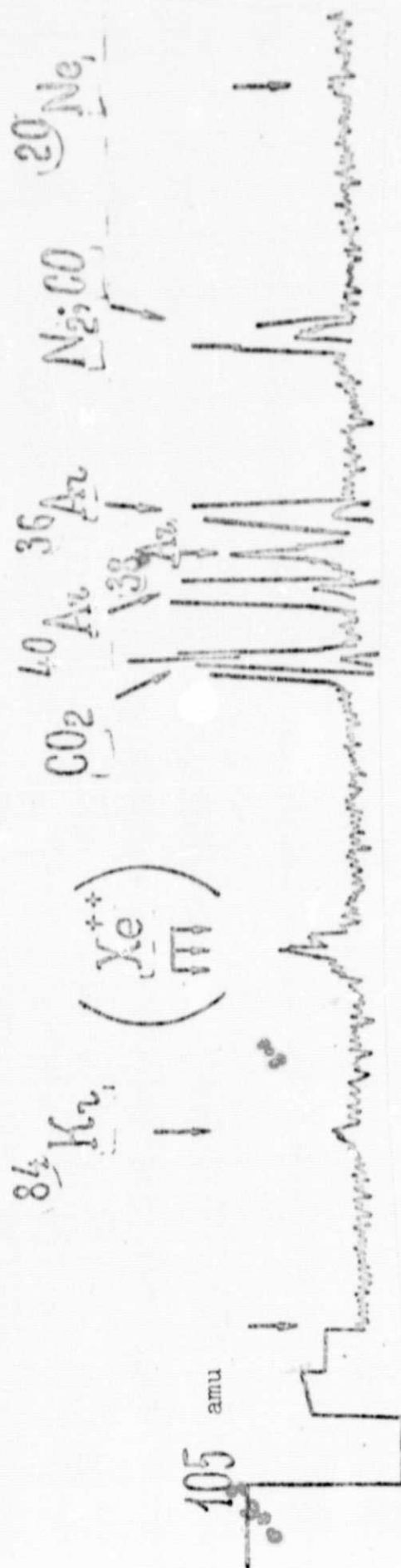


Figure 3. A fragment of a mass-spectrum in the field 20-105 amu obtained in analysis regime for inert gases with increased sensitivity (Venera-11). Peaks of isotopes of argon are clearly visible and it is clear that the isotope composition of argon is sharply "abnormal." Mass peaks of neon-20 and krypton-84 are visible at the limit of sensitivity.

of both "primary" isotopes of argon in the atmosphere of Venus, on the other hand, agrees well with the isotopes of argon in Earth's atmosphere.

More precise values of the relative abundance of argon isotopes in the atmosphere of Venus are:

A36	42 \pm 2%
A38	8 \pm 2%
A40	50 \pm 2%
Total:	100%

The total content of the argon isotope is evaluated preliminarily equal to 150 \pm 50 ppm.

The content of the neon isotope (Ne20) is from 10 to 15 ppm, and Krypton Kr84--from 0.5 to 0.8 ppm.

In the spectrum presented in Figure 3, besides the components of argon, neon, krypton and fragmentary peaks of CO and CO₂ already named, there is a group labeled (Xe⁺⁺). This is xenon, introduced into the instrument for technological purposes, it is the reference point of the mass scale.

Measurements of the total abundance of argon isotopes on the Venera-11 and Venera-12 agree satisfactorily with the data of Hoffman et al. (1979) obtained on the Pioneer-Venus mission for a large probe and agree well with the data of Von-Tsan et al. (1979) which measured argon isotopes on equipment flown in the same experiment:

	Abundance, ppm			
	A36	A38	A40	Total
Hoffman <u>et al.</u> 1979	100	20	120	240
Von-Tsan <u>et al.</u> 1979	80	-	80	160
Venera-11, 12	63	12	75	150 \pm 50

Unfortunately, there are strong disparities in the estimates of the abundance of neon. According to Hoffman's data, it amounts to 100 ppm; according to the data of Von Tsan et al., it is from 100 to 200 ppm while our data definitely are on the order of the lower values--from 10 to 15 ppm which is convincingly, as has been presented, demonstrated by the mass-spectra obtained, one of which is reproduced in Figure 3.

The absence among American authors of mass-spectrometer data on the content of nitrogen both in the lower atmosphere of Venus and in the thermosphere (Hoffman et al., 1979, Von Tsan et al., 1979) is still unclear. Our data on nitrogen clearly agree with the results of the first analysis by a gas chromatograph on the large probe of the Pioneer-Venus although the authors themselves (Oyama et al., 1979) consider the third chromatographic analysis more reliable.

Further progress in processing the data obtained involves **making a new series of calibrations** with the remaining instruments like the processing of the mass-spectra on an EVM [Elektronnaya vychislitel'naya mashina, electronic computer] as a result of which the level of noise interference will be decreased. One can expect that there will be a decrease in error in certain absolute abundances of all the components named, a more precise interpretation of "excesses" of mass-peaks with $M = 17, 18$ and 32 amu, and also a more precise isotope composition of "basic" components of the atmosphere of Venus--carbon, oxygen and nitrogen. /10

The following persons successfully set up and carried out this work at different stages of its development: M.A. Berezhkovskiy, S.V. Vasyukov, I.A. Kalinina, V.G. Klimovitskiy, G.N. Levina, M.L. Libman, L.N. Ozerov, V.A. Pavlenko, V.G. Perminov, M. Ye. Slutskiy, S.I. Torbin, I.I. Chemeris, V.F. Shkurdoda, Yu. A. Shul'chishin, O.N. Yakovlev and many, many other colleagues and comrades. The authors wish to express their deep appreciation to them.

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